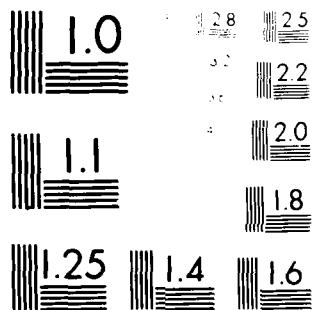


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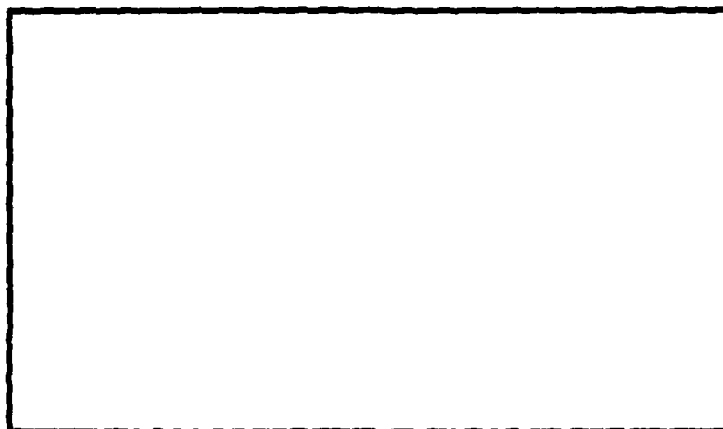


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AN ULTRASENSITIVE ELECTRON (SOFT  
X-RAY) SILVER HALIDE/CHALCOGENIDE  
NEGATIVE OR POSITIVE INORGANIC RESIST

Final Report

Prepared by:

Jerome M. Lavine

December 1981

GCA CORPORATION  
GCA/TECHNOLOGY DIVISION  
Bedford, Massachusetts

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## SECTION 1

### INTRODUCTION

#### WORK OF FIRST YEAR

In the first annual report we provided the background and described some of the available but not completely satisfactory models of Ag photodoping. We described our work with evaporated AgBr/As<sub>2</sub>S<sub>3</sub>, noting that the system had extremely high sensitivity in the deep UV, at e-beam and x-ray wavelengths. We reported sensitivities of the order of 50  $\mu\text{J}/\text{cm}^2$  at 260 nm and roughly the same at 7 Å. We reported e-beam sensitivities of the order of  $10^{-9}$  C/cm<sup>2</sup> at voltages ranging from a few keV to 20 keV. We described the resolution problem, showed a technique for decreasing grain size by adding AgI to the melt, and showed that the whisker-type development growth of Ag was the limiting factor in achieving better resolution. We described the sensitization of the surface of As<sub>2</sub>S<sub>3</sub> with a film derived from evaporated AgBr and showed that this system exhibited a photographic inversion effect. We showed lithographic results with As<sub>2</sub>S<sub>3</sub>, with Ag/As<sub>2</sub>S<sub>3</sub>, with AgBr/As<sub>2</sub>S<sub>3</sub> and with surface-sensitized As<sub>2</sub>S<sub>3</sub>.

During the second year of this contract we focused on the Ag/As<sub>2</sub>S<sub>3</sub> system with potentially greater resolution capability unlimited by developmental gain but with concomitantly lower speed limited by a one-photon-one-event-type of photosensitivity. During this period we focused upon obtaining high gamma to achieve high resolution lithography (as for the VHSIC Program namely, 0.5 micron linewidths) using conventional UV lithographic equipment. A second focus was on photographic techniques for achieving higher speed for this system. We obtained gamma in excess of 10 at UV wavelengths with Ag/As<sub>2</sub>S<sub>3</sub> which permits 0.5 micron lines with a 436 nm step-and-repeat lithographic system. Our speed enhancement techniques allow us to expose in the 10-20 mJ/cm<sup>2</sup> range. This will be described in detail below.

#### MAIN THRUST FOR SECOND YEAR

The use of evaporated AgBr to generate a photographic Ag image provided high speed, at least a factor of 100 improvement over the conventional Ag-photodoping, and provided high absorption to deep UV, e-beam and x-radiation. While each of these lithographic media required improved resist sensitivity, the combination of a long-term program to solve the resolution limitation due to infectious development and the possibility of achieving 0.5 micron lithography with UV optical exposures in the short term motivated a shift in direction.

It was already clear that the Ag/chalcogenide inorganic resist system was capable of high gamma and that high gamma would enable us to extend the high-frequency performance of an optical system. We present this argument below.

The Modulation Transfer Function is a convenient measure of the high-frequency performance of an optical system. Figure 1 shows the MTF of a Zeiss high quality lens system as currently used, for example, in the GCA DSW 4800. The MTF may be defined as follows:

$$MTF = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} \quad (1)$$

where  $I_{\max}$  and  $I_{\min}$  are the maximum and minimum amplitudes of the light after the system output has passed through a mask consisting of equal lines and spaces. For very large geometries  $I_{\min} \rightarrow 0$  and  $MTF \rightarrow 1$  since all radiation is effectively blocked in regions corresponding to the opaque areas. As the line widths are reduced, diffraction and other detrimental effects introduce light into the opaque regions. This reduction in contrast then reduces the modulation transfer function below unity. Ultimately, when the light in the opaque regions equals the light in the exposed regions, the MTF goes to zero.

Figure 2 shows the characteristic curve of a sample of  $As_2S_3$ . The slope of this curve is the gamma or contrast of the resist. It is possible to define a function which takes into account the gamma of the resist only and describes the match between the optical system and the resist. This so-called Resist Modulation Transfer Function does not include the influence of any asymmetries due to edge effects and thus is not a true measure of the high-frequency performance of the resist. The RMTF is defined

$$RMTF = \frac{E_{100} - E_0}{E_{100} + E_0} \quad (2)$$

where  $E_{100}$  is the minimum exposure energy for 100 percent of the resist remaining, and  $E_0$  is the maximum exposure for zero resist remaining. The RMTF of a resist is related to the gamma of the resist as follows:

$$RMTF = \frac{10^{1/\gamma} - 1}{10^{1/\gamma} + 1} \quad (3)$$

The requirement for obtaining a resolvable feature then becomes:

$$MTF \geq RMTF \quad (4)$$

This condition implies that, for an MTF greater than zero, it is always possible to find a gamma such that the unwanted radiation does not register on the film. In the case of conventional photopolymers with gamma of the order



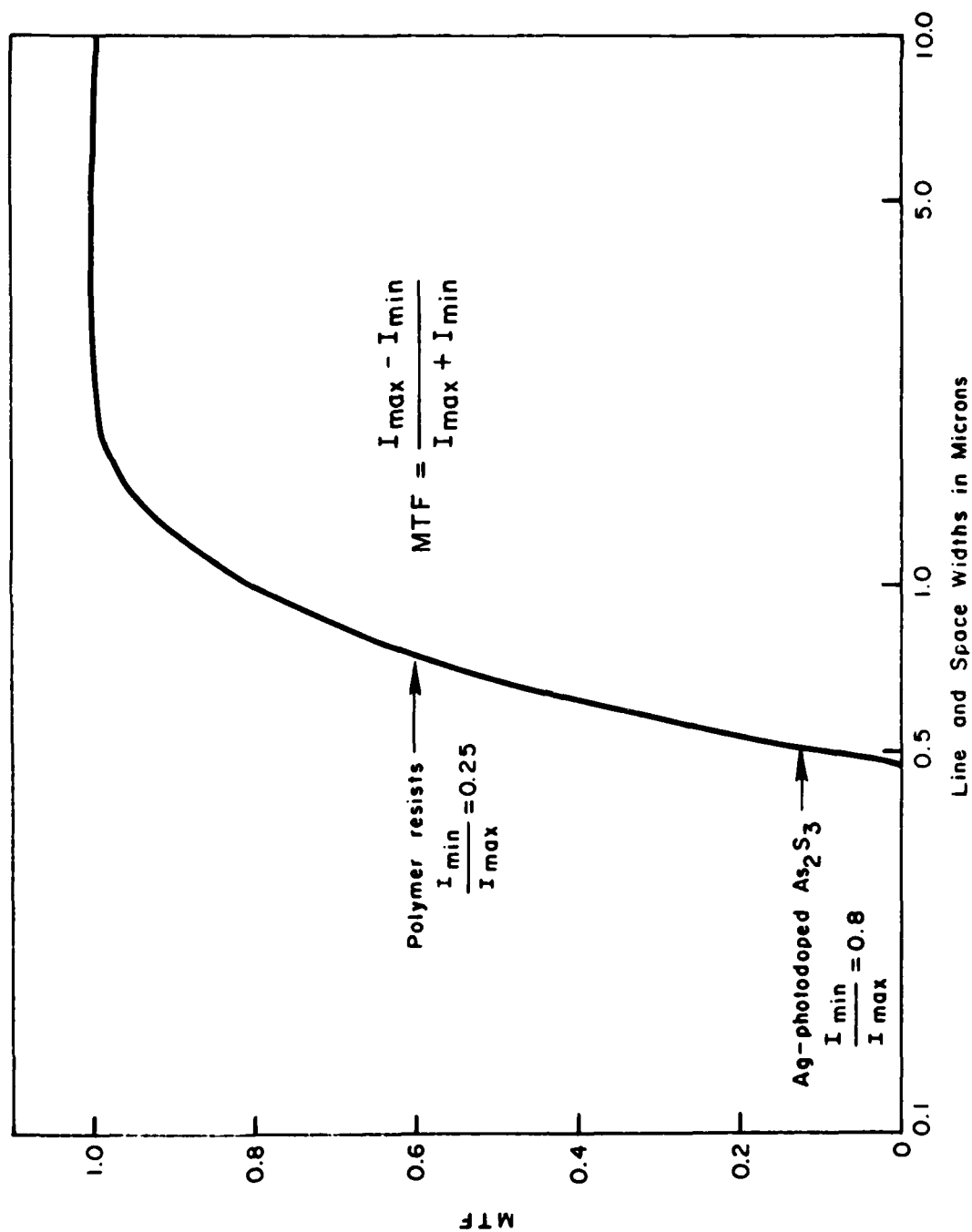


Figure 1. The modulation transfer function of a Zeiss high quality lens (10x) in a step-and-repeat system.

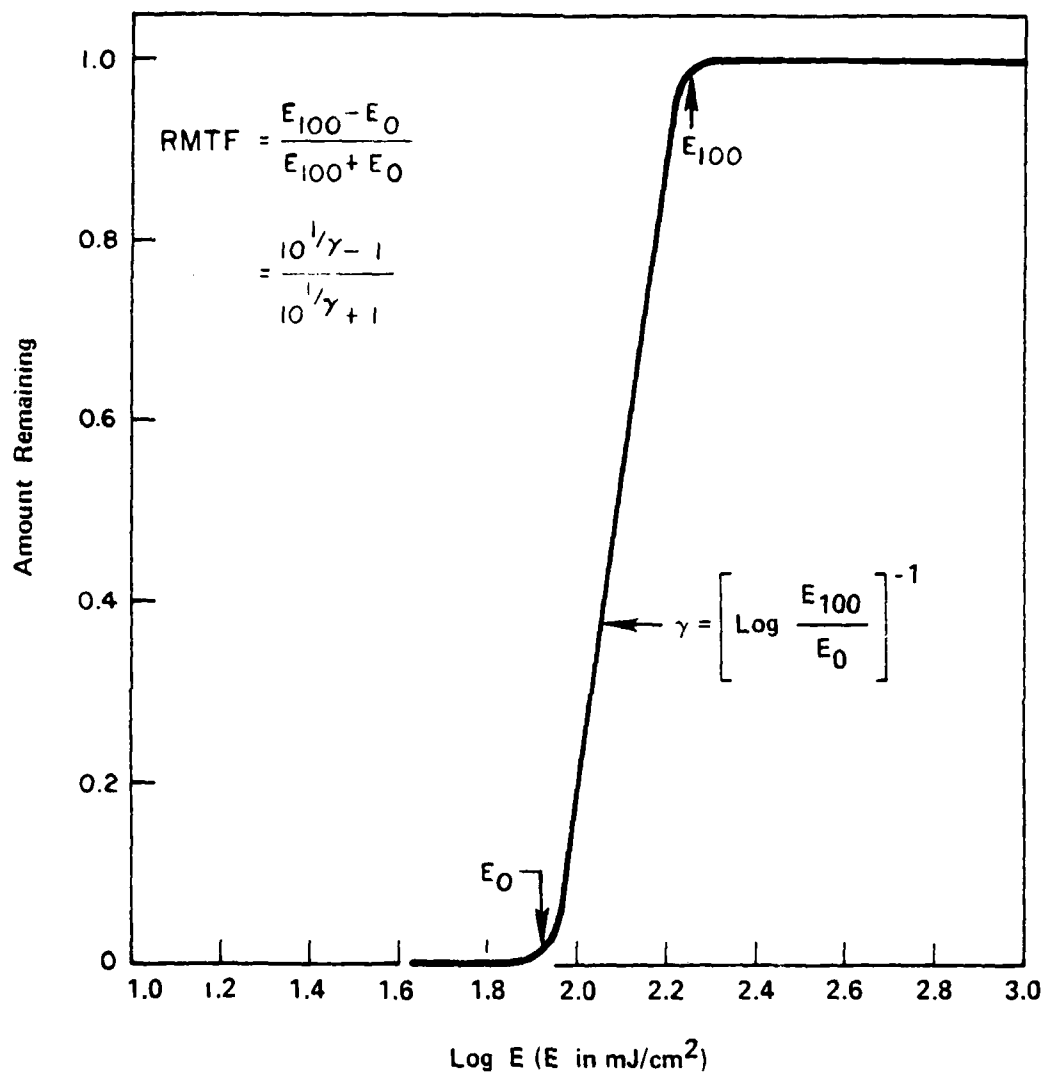


Figure 2. Fraction of As<sub>2</sub>S<sub>3</sub> remaining after development (etching) as a function of incident energy density.

of 2, line widths corresponding to MTF values of 0.6 may be resolved. For the optical system of Figure 1, this translates to lines of the order of 0.8 micron. In the case of Ag/As<sub>2</sub>S<sub>3</sub> with gamma of the order of 10 or even greater, high-frequency performance may be extended to MTF~0.1 and line widths of 0.5 micron or smaller.

In Figure 3 we show a block diagram of the Ag-photodoping process. At the present time there is no completely satisfactory explanation for the high-speed collinear penetration of Ag into the As<sub>2</sub>S<sub>3</sub> under the action of bandgap light. The favored suggestion is that under the action of light a photochemical specie or species is formed as suggested by Malinowski's<sup>1</sup> tarnishing reaction. However, there is suggestion<sup>2</sup> that Ag<sub>2</sub>S is not the only possible constituent formed under the action of the light. In the absence of a completely acceptable model it was essential that we empirically examine those variables contributing to the lithographic process.

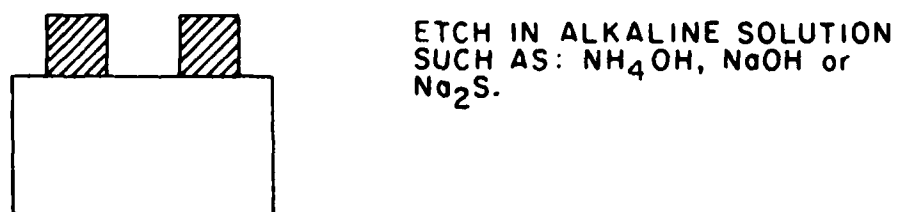
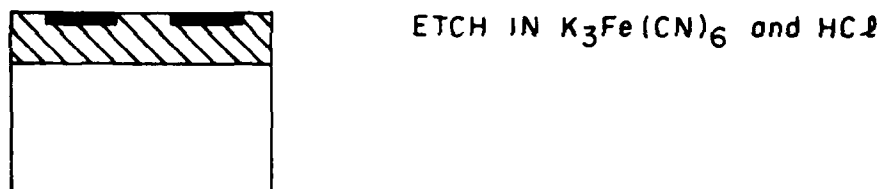
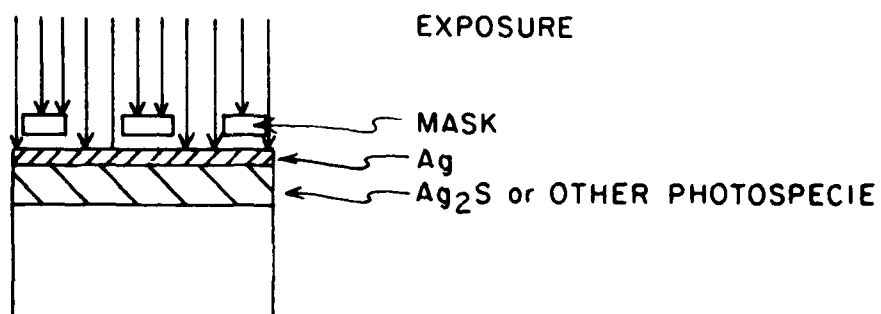
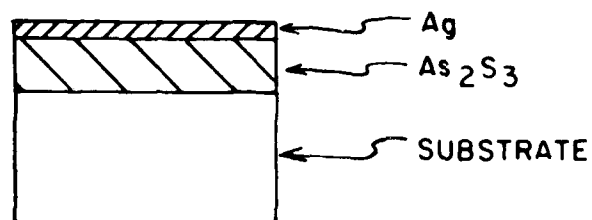


Figure 3. Block diagram of Ag photodoping process.

## SECTION 2

### EXPERIMENTAL

#### Ag DEPOSITION

The composition and thickness of the deposited Ag layer plays an important role in the doping process. The early workers<sup>3,4</sup> in the field reported on deposition from  $\text{AgNO}_3$ . We tried deposition from various concentrations of  $\text{AgNO}_3$ . We also tried deposition from  $\text{KAg}(\text{CN})_2$  at various temperatures. It was very early established that the thickness of the Ag was an important parameter if for no other reason than excessive thickness would not permit light transmission. Figure 4 shows a plot of gamma as a function of plating time, essentially film thickness, from a  $\text{KAg}(\text{CN})_2$  solution at  $65^\circ\text{C}$ . This curve clearly points out the need for an adequate and uniform thickness of Ag. We also used evaporation as a deposition technique. In Figure 5 we show SEM photographs of Ag films obtained (5a) by electroless Ag plate in  $\text{KAg}(\text{CN})_2$  at  $65^\circ\text{C}$  and (5b) by evaporation. These photographs clearly point out the desirability of using evaporation to secure a uniform film. The electroless plating technique also gave difficulty in thickness control. We therefore now use Ag-evaporation as our standard technique.

#### ETCHING (DEVELOPMENT)

The data of Figure 4 were obtained by etching in  $\text{NH}_4\text{OH}$ . The highest gamma that we could obtain in this etchant was a gamma of the order of 4. In most photographic systems gamma depends critically upon the developer and the time of development. The same obtains for the Ag/ $\text{As}_2\text{S}_3$  system. We shall first describe our experimental results and in the next section we shall demonstrate a simple mathematical model which supports these observations.

We first tested most of the common alkaline etchants in various concentrations and then moved onto other systems. Figure 6 shows the behavior of a few of the etchants we tried. Gamma measurements were made by exposing large areas to essentially broadband Hg light with energy density of the order of  $1.5 \text{ mJ/cm}^2$ . The removal of the  $\text{As}_2\text{S}_3$  was monitored by measuring optical density. To date,  $\text{Na}_2\text{S}$  has provided us with the highest gammas, greater than 10. Figure 7 shows the result of two exposures on the same run of materials using  $\text{Na}_2$  as the etchant. Figure 8 shows the increase of gamma with increase of etchant time.

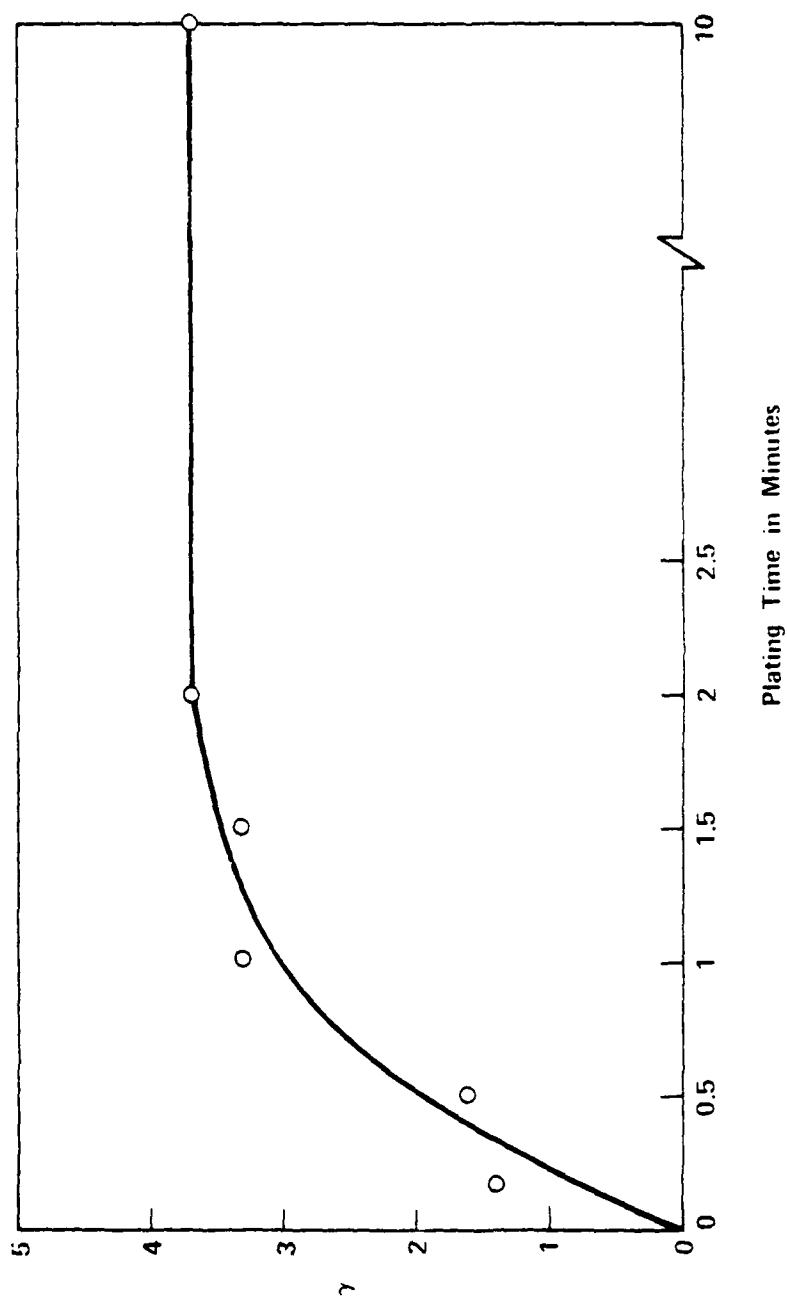


Figure 4.  $\gamma$  of Ag photodoped  $\text{As}_2\text{S}_3$  as a function of plating time.  
Plating solution,  $\text{KAg}(\text{CN})_2$  at  $65^\circ\text{C}$ ; etchant,  $\text{NH}_4\text{OH}$ .

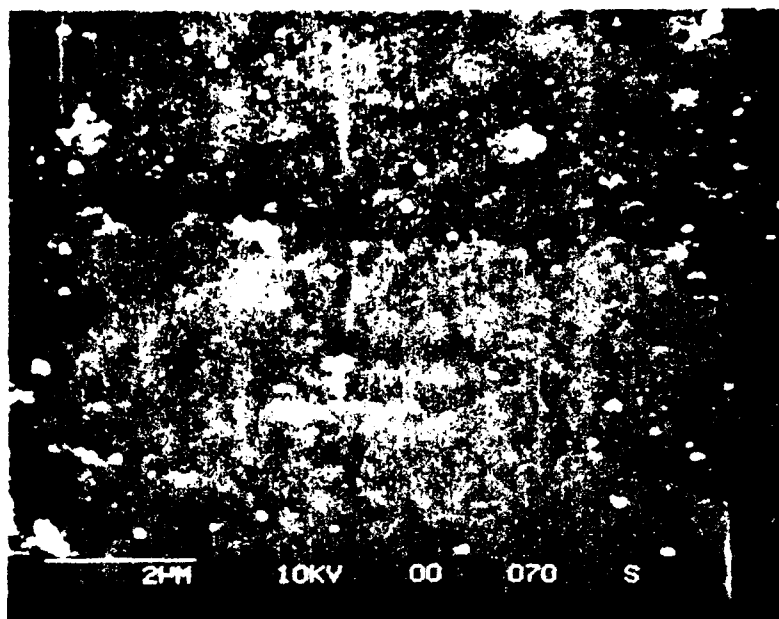


Figure 5a. SEM of surface of  $\text{As}_2\text{S}_3$  with Ag deposited from  $\text{KAg}(\text{CN})_2$  ( $\sim 200 \text{ \AA}$ )

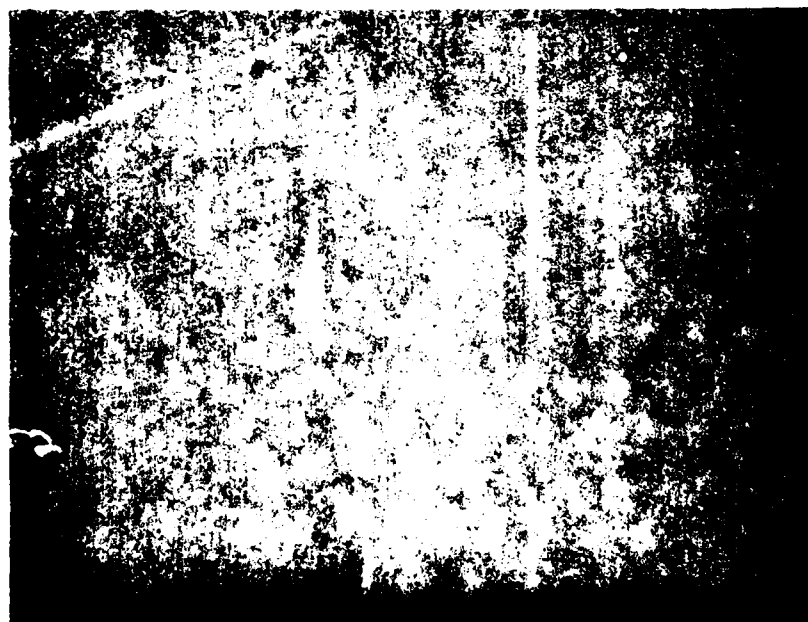


Figure 5b. SEM of surface of  $\text{As}_2\text{S}_3$  with Ag deposited by evaporation ( $\sim 200 \text{ \AA}$ )

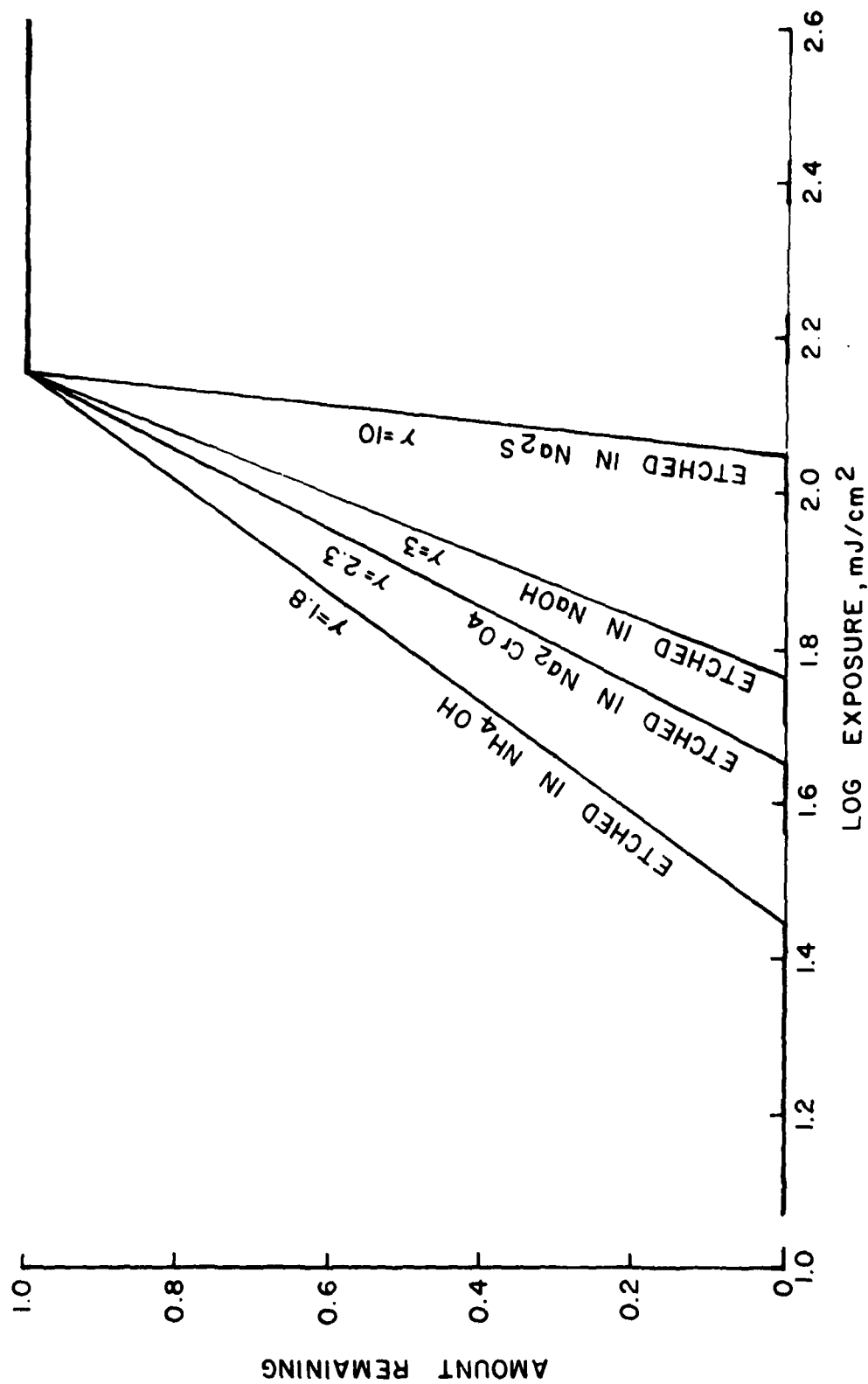


Figure 6. Variation of  $\gamma$  with etchant.



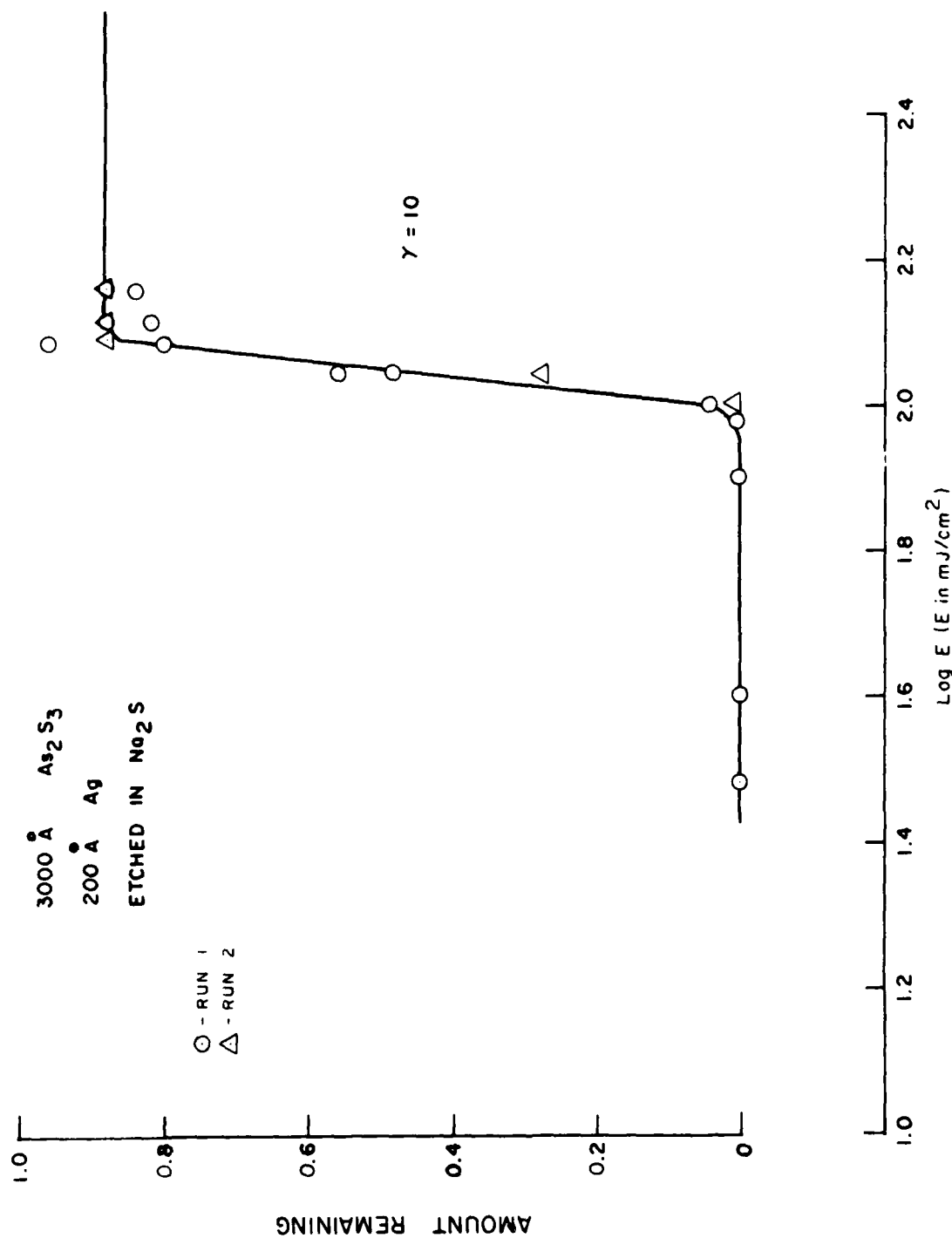


Figure 7. Amount remaining as a function of log exposure of an Ag-photodoped  $\text{As}_2\text{S}_3$  film after etching in  $\text{Na}_2\text{S}$ .

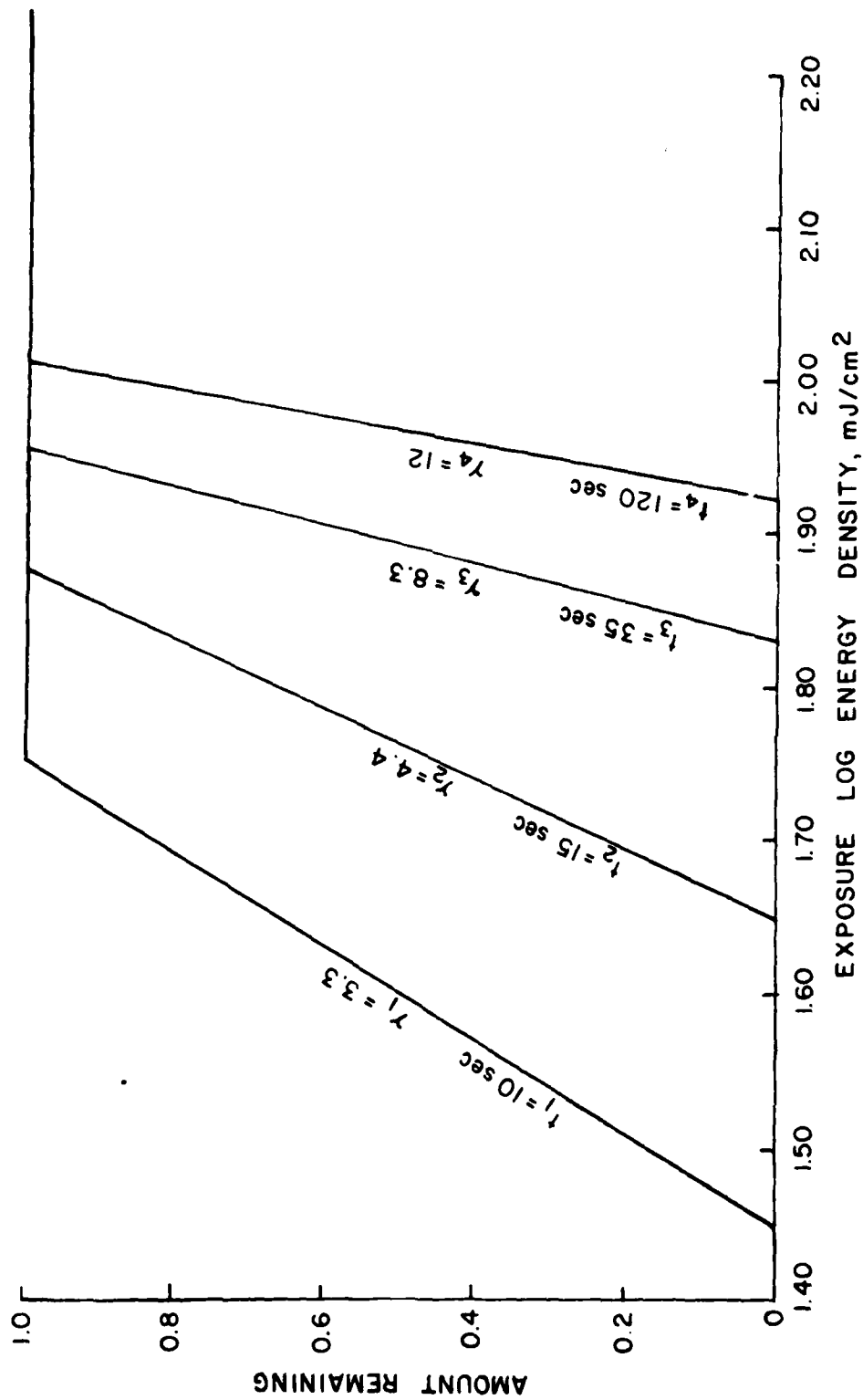


Figure 8. Variation of  $\gamma$  with etching time: 1000A  $\text{As}_2\text{S}_3$ , 70Å Ag, etched in  $\text{Na}_2\text{S}$ .

# SIMPLE MODEL

It has been shown in three different laboratories that Ag-photodoping is a three-step process. By measuring the penetration of Ag into the  $\text{As}_2\text{S}_3$  Goldschmidt and Rudman,<sup>5</sup> Buroff and Baeva<sup>6</sup> and recently Kostyshin and Ushenin<sup>7</sup> have shown that there is an incubation exposure with no change in the Ag concentration which Goldschmidt calls a radiation damage. Then there is a dissolution of the Ag film at a constant rate which has been ascribed as an interface reaction and finally a third step which proceeds at the square-root of time and is the so-called penetration step. It is this third step which we assume provides the insolubilization of the  $\text{As}_2\text{S}_3$  by generating a distribution of Ag throughout the bulk, although the reaction products at the surface may very well contribute. We may therefore postulate that after an initial time  $t_0$  the Ag diffuses into the  $\text{As}_2\text{S}_3$  with a  $t^{1/2}$  dependence.

Since we are dealing with a constant light exposure, the penetration of Ag into the  $\text{As}_2\text{S}_3$  may be equated to  $E$ , the energy density by

$$\delta = \alpha(E - E_{\text{incubation}})^{1/2} \quad (5)$$

and if we shift the origin in time or energy we may express the penetration as

$$\delta = \alpha E^{1/2} \quad (6)$$

In Figure 9 we show a composite plot of the penetration depth as a function of Log energy density with ordinate on the left and origin at the top, and the characteristic curve of  $\text{As}_2\text{S}_3$  with ordinate on the right and origin at the bottom.

As we indicated above, we delineate the characteristic curve by exposing over a range of energy densities and etching for a time,  $\tau$ . For an exposure  $E_0$ ,  $\delta(E_0) = ab$  (photodoped thickness) of Figure 9 and  $bc$  is thus undoped thickness in the exposed area, where the total  $\text{As}_2\text{S}_3$  thickness is  $D$ . We set the etching time  $\tau = \tau_1 + \tau_2$  where  $\tau_2$  = the etching time of the undoped  $\text{As}_2\text{S}_3$  and  $\beta_1$  = the etching rate and  $\tau_1$  = the etching time for the Ag-doped  $\text{As}_2\text{S}_3$  and  $\beta_0$  = the etching rate.

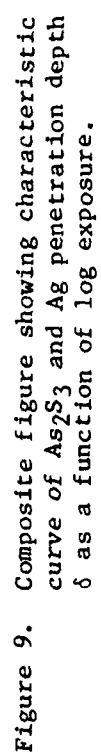
$$\delta(E_0) = \alpha E_0^{1/2} = \beta_1 \tau_1 \quad (7)$$

where  $E_0$  is the largest exposure that results in zero remaining thickness after etching.

$$D - \alpha E_0^{1/2} = \beta_0 \tau_2 \quad (8)$$

From Equation (8) and with  $\tau = \tau_1 + \tau_2$

$$D - \alpha E_0^{1/2} = \beta_0 (\tau - \tau_1) \quad (9)$$



Substituting from Equation (7),  $\tau_1 = \frac{\alpha E_o^{1/2}}{\beta_1}$

$$D - \alpha E_o^{1/2} = \beta_o \left( \tau - \frac{\alpha E_o^{1/2}}{\beta_1} \right) \quad (10)$$

$$\beta_o \tau = \alpha E_o^{1/2} \left( \frac{\beta_o}{\beta_1} - 1 \right) + D \quad (11)$$

Now if we were to etch for exactly the time it takes to remove the unexposed material, this time  $\tau_o$  is given by

$$D = \beta_o \tau_o \quad (12)$$

However, we always etch for time  $\tau$ , such that  $\tau > \tau_o$ . If we divide both sides of Equation (11) by Equation (12)

$$\frac{\tau}{\tau_o} = \frac{\alpha E_o^{1/2}}{D} \left( \frac{\beta_o}{\beta_1} - 1 \right) + 1 \quad (13)$$

Transposing and squaring we obtain

$$E_o = \left( \frac{D}{\alpha} \right)^2 \frac{(\tau/\tau_o - 1)^2}{(\beta_o/\beta_1 - 1)^2} \quad (14)$$

To calculate  $E_{100}$ , we have etched through  $\delta = \alpha E_{100}^{1/2}$  in time  $\tau$  such that

$$\beta_1 \tau = \alpha E_{100}^{1/2} \quad (15)$$

Dividing by  $D = \beta_o \tau_o$ , we obtain

$$E_{100} = \left( \frac{D}{\alpha} \right)^2 \left( \frac{\beta_1}{\beta_o} \right)^2 \left( \frac{\tau}{\tau_o} \right)^2 \quad (16)$$

For any  $E$  such that  $E_o < E < E_{100}$  we have

$$\delta(E) = \alpha E^{1/2} = \beta_1 \tau_1 \quad (17)$$

The amount remaining is given by  $d$ , i.e., this is the material not etched away and appearing in the r.h.s. ordinate of Figure 9. Then the undoped material etched away at rate  $\beta_0$  in time  $\tau_2$  is

$$D - d - \delta(E) - d = \beta_0 \tau_2 \quad (18)$$

Again

$$\tau = \tau_1 + \tau_2 \quad (19)$$

where  $\tau_1$  = etching time for the Ag-doped and

$\tau_2$  = etching time for the undoped.

$$D - d - \alpha E^{1/2} = \beta_0 (\tau - \tau_1) \quad (20)$$

Again dividing by  $D = \beta_0 \tau_0$  and substituting  $\tau_1 = \frac{\alpha E^{1/2}}{\beta_1}$

$$1 - \frac{d}{D} = \frac{\alpha}{D} E^{1/2} + \frac{\tau}{\tau_0} - \frac{\beta_0}{\beta_1} \alpha E^{1/2} \quad (21)$$

$$\frac{d}{D} = 1 - \frac{\tau}{\tau_0} - \frac{\alpha}{D} \left(1 - \frac{\beta_0}{\beta_1}\right) E^{1/2} \quad (22)$$

Multiplying and dividing by Equation (16) we obtain

$$\frac{d}{D} = 1 - \left[ 1 - \left( \frac{\beta_0}{\beta_1} - 1 \right) \left( \frac{E}{E_{100}} \right)^{1/2} \right] \frac{\tau}{\tau_0} \quad (23)$$

From the foregoing equations we can see that

1. The maximum value of  $\frac{d}{D} = 1 - \left[ 1 - \left( \frac{\beta_0}{\beta_1} - 1 \right) \right] \frac{\tau}{\tau_0}$
2. Gamma may be obtained from Equations (14) and (16).

$$\gamma = \left[ \log \frac{E_{100}}{E_0} \right]^{-1} \quad (24)$$

$$\gamma = \left[ \log \frac{\left(\frac{D}{\alpha}\right)^2 \left(\frac{\beta_1}{\beta_0}\right)^2 \frac{t}{t_0}}{\left(\frac{D}{\alpha}\right)^2 \frac{\left(\frac{t}{t_0} - 1\right)^2}{\left(\frac{\beta_0}{\beta_1} - 1\right)^2}} \right]^{-1} \quad (25)$$

$$= \left[ 2 \log \frac{1 - \frac{\beta_1}{\beta_0}}{1 - \frac{t}{t_0}} \right]^{-1} \quad (26)$$

Therefore, the smaller the ratio  $\beta_1/\beta_0$  the higher the gamma. From Equation (26) we also note that gamma increases with increasing etching time.

#### SPEED ENHANCEMENT TECHNIQUES

Our first effort at speed enhancement involved the use of evaporated AgBr deposited on the  $As_2S_3$ . This effort was described in our First Annual Report. The second method also involved a photographic technique and is shown in the block diagram of Figure 10. In this procedure we evaporate our standard thickness of Ag onto 3000 Å of  $As_2S_3$ . We expose at one-tenth of the conventional exposure energy density. We then remove the excess Ag and photochemical species in  $K_3Fe(CN)_6$  and HCl. The sample is then placed in a physical developing solution. This is essentially an electroless Ag plating solution with properties that result in Ag deposition only in select areas, namely in previously imaged areas containing either Ag or  $Ag_2S$ . An amount of Ag is selectively deposited from the physical developer to provide insolubilization when photodoped into the  $As_2S_3$ . This additional Ag is then photodoped with flood radiation at no additional expense to the photographic process. The details of this procedure are given in Appendix A which contains excerpts of a patent disclosure filed on this process.

In Figure 11 we show the photographic speed of the several systems covered during this 2-year program. The slope of the curve does not truly represent the gamma of the process but rather simply spans the region of sensitivity. Evaporated AgBr/ $As_2S_3$  has a sensitivity of the order of 1-10 mJ/cm<sup>2</sup> to broadband Hg light. The speed-enhancement technique with a gain of about 10 reduces our standard 125 mJ/cm<sup>2</sup> 200 Å Ag/3000 Å  $As_2S_3$  speed to 15-20 mJ/cm<sup>2</sup>. The  $S^2$  process exhibited a speed of 30-35 mJ/cm<sup>2</sup>. Shown on the same figure is the speed of AgBr evaporated onto a suitable subbing materials and  $As_2S_3$  which exhibits very small differential etching between exposed and unexposed regions.

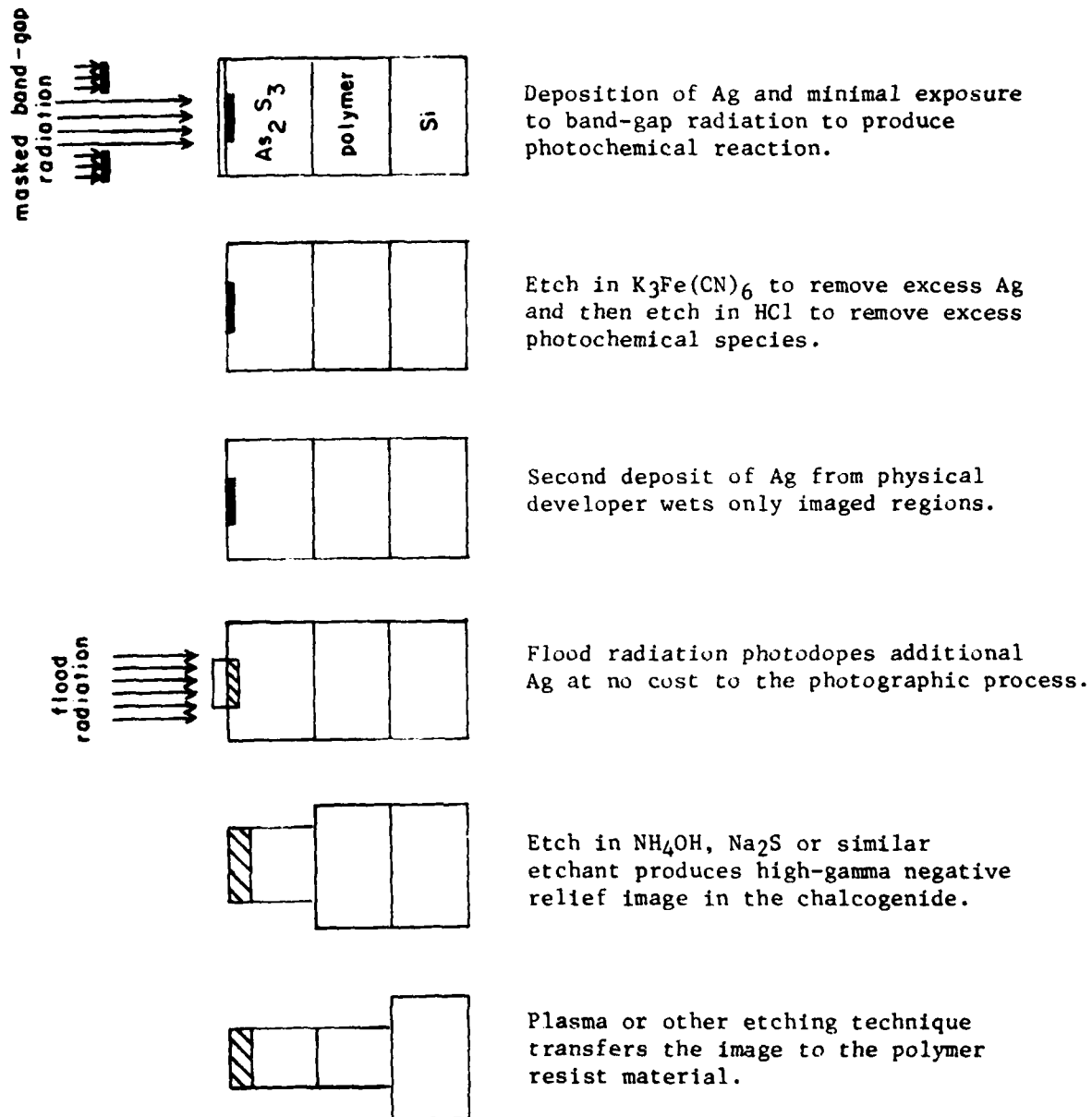


Figure 10. Block diagram of the speed-enhancement technique.



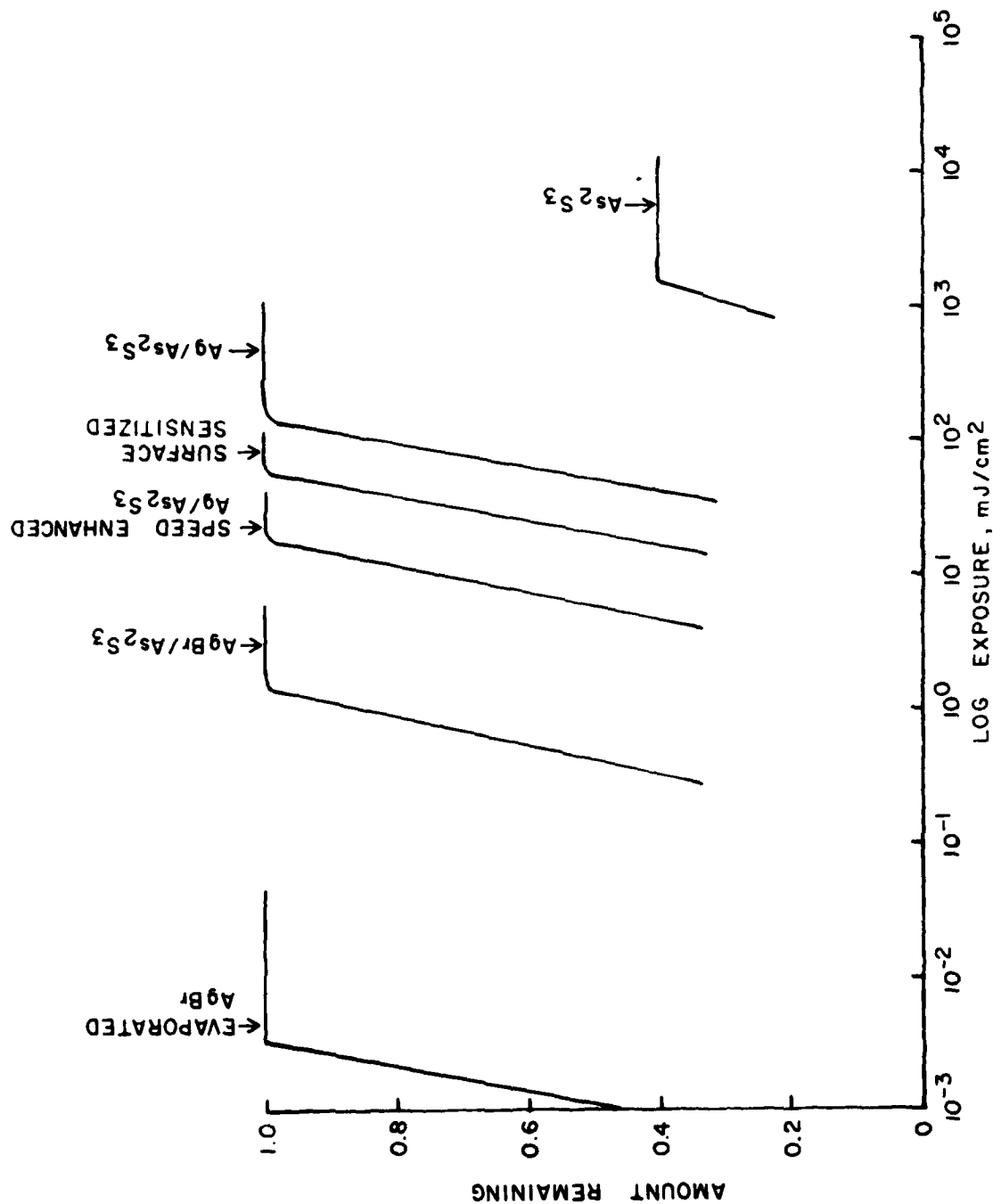


Figure 11. Comparison of sensitivity of the several processes.

### SECTION 3

#### RESULTS

During the period of this program we have shown:

1. That a photographic Ag image could be obtained from evaporated AgBr. That this image could be photodoped into the  $\text{As}_2\text{S}_3$  with flood radiation without degradation of resolution.
2. That the AgBr/ $\text{As}_2\text{S}_3$  system, because of the large gain in development and because of the large absorption exhibits the highest photosensitivity yet observed in the deep UV at e-beam and x-ray wavelengths.
3. That the resolution limitation of this system, with our present technology was about 1 micron, but that an appropriate attack upon infectious development could improve this by a large factor. (The work of Malinowski's group at the Bulgarian Academy of Sciences has just been published<sup>8</sup> and they report development techniques capable of achieving 0.3 micron lines with evaporated AgBr.)
4. We showed that it was possible to Ag-photodope with a very thin layer of Ag or  $\text{Ag}_2\text{S}$  and to achieve an image at about  $30 \text{ mJ/cm}^2$  in our  $\text{S}^2$  process described in the First Annual Report.
5. We demonstrated a technique for enhancing the speed of the Ag-photodoping process by about a factor of 10. This is fully described in Appendix A.
6. We showed that significant variation in gamma occurred with etchant and pointed out that  $\text{Na}_2\text{S}$  provided high gamma of the order of 10 or more.
7. During the period of this contract we have published or presented the following papers:
  - G. M. Goldberg, J. M. Lavine, J. I. Masters, P. A. Thompson and Z. Y. Vayman, Technical Digest, IEEE IEDM, Washington, DC, December 1979, Abstract No. 3.7, p. 62.
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- J. M. Lavine, J. I. Masters and A. Das, "A Multilayer Photoresist System for Submicron Imaging Employing Evaporated AgBr as the Photosensitive Layer for Deep UV, E-beam and X-ray Lithography," Second International Symposium on Model Investigations of the Photographic Process and New Photoregistering Systems, Drouzhba, Bulgaria, September 1980.
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## SECTION 4

### CONCLUSIONS

It is our firm conclusion that the Ag/chalcogenide system can provide better high-frequency performance under UV excitation by virtue of its large gamma than a polymer system. The Ag/chalcogenide system has already shown the capability of providing the 0.5 micron linewidths required by the VHSIC Program using 436 nm Step-and-Repeat UV lithography. We believe that with a better understanding of the mechanism involved in Ag-photodoping important improvements will be forthcoming.

The possibility of obtaining reasonably high speed in this system is good, making use of only the fundamental parameters of Ag-photodoping. Speed-enhancement techniques can greatly decrease exposure energy density in addition. Nor should evaporated AgBr be ignored. There is at present no other system capable of the amplification available in the AgBr system. We firmly believe that additional research in this area would be profitable.

Our overall conclusion is that inorganic photosensitive films will play an important role in the microlithography of the future.

## SECTION 5

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SECTION 6

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APPENDIX A  
PORTIONS OF PATENT

TITLE

Resist System Having Increased Light Response.

INVENTOR

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GENERAL NATURE OF THE INVENTION

The present invention includes a chalcogenide resist system having sharply increased response to activating radiation, wherein a chalcogenide layer is formed on a suitable substrate which may be a mask support substrate, the semiconductor wafer itself, or other suitable substrate. In the preferred embodiment of the invention the chalcogenide layer is vacuum evaporated onto the substrate, and the invention includes improved vacuum evaporation of the chalcogenide. In addition, in the preferred embodiment of the invention, use is made of the so-called two layer system in which the chalcogenide is itself placed on a suitable resist layer on the substrate.

After the chalcogenide is formed on the substrate, a weak silver image is formed thereon, the image being insufficient for conventional photodoping methods. The image is then increased through the deposition of additional silver or silver substance, after which it is driven into the chalcogenide for example by flooding techniques to form a differential etch-resistant pattern. The chalcogenide layer is then etched by known methods to form a pattern corresponding to the desired semiconductor pattern.

According to one procedure for carrying out the present invention, a layer of a chalcogenide such as  $As_2S_3$  or a GeSe chalcogenide is vacuum evaporated onto a substrate at a relatively low temperature and at a relatively slow and uniform rate to form a chalcogenide layer of increased response. A silver layer is deposited thereon by chemical reduction of a silver salt onto the chalcogenide or by vacuum evaporation of silver thereon. This silver layer is then exposed to a pattern of activating radiation and the background silver removed, leaving a silver image corresponding to the desired pattern.



It is then treated with a silver-containing agent capable of depositing silver or silver sulfide on the image areas. A solution of  $\text{NaAgSO}_3$  in the presence of activating radiation is the presently preferred agent. This image, now containing additional silver, is exposed to suitable radiation such as collimated band-gap radiation to drive the silver into the chalcogenide to form etch-resistant chalcogenide areas corresponding to the silver areas.

#### SPECIFIC DESCRIPTION OF THE INVENTION

The nature of the invention is best illustrated in conjunction with a specific Example setting forth a presently preferred procedure for carrying out the invention.

##### Example 1

A chalcogenide pattern is placed on a semiconductor wafer according to the following procedure. A polymer resist layer is placed on a semiconductor wafer surface by conventional procedures, using a thin layer of Hunt Waycoat IC 43 Negative Resist which is spun onto the wafer surface and baked at about  $200^\circ\text{C}$  for half an hour. The resist-coated wafer is placed in a vacuum evaporator and preliminary degassed by evacuating the evaporator to a pressure of about  $4 \times 10^{-6}$  Torr and holding the pressure at the level for about 10 minutes.

A molybdenum boat containing arsenic trisulfide is positioned in the evaporator about 1 foot from the position of the wafer. The boat temperature is slowly raised to a temperature of about  $350^\circ\text{C}$ , the temperature being monitored by the rate of evaporation. Arsenic trisulfide is evaporated onto the wafer surface at a steady rate of about 1 Å per second to form a layer about 3000 Å thick. After the desired layer of arsenic trisulfide is deposited, the pressure is released and the coated wafer is removed from the evaporator.

The chalcogenide-coated wafer is then coated with a layer of metallic silver; in this case a layer of silver is formed on the wafer by dipping it for 2 or 3 minutes in a solution of  $\text{NaAgSO}_3$  of the same composition as that of the developing solution described hereinafter.

The wafer, now coated with chalcogenide and silver on the polymer resist surface is then exposed to a pattern of activating radiation, employing about  $5 \text{ mJ}/\text{cm}^2$  as a measure of exposure of the image areas, compared with an exposure level of about 100 to  $200 \text{ mJ}/\text{cm}^2$  which is a conventional exposure level for such an element. Background silver is then removed with a first bath of  $\text{K}_3\text{Fe}(\text{CN})_6$  plus  $\text{KBr}$ , which converts the background silver to  $\text{AgBr}$ , followed by a photographic fixer and a dip in concentrated  $\text{HCl}$ .

The wafer at this point in the process contains a weak pattern of silver on or in the chalcogenide layer, the pattern being insufficient to provide a chalcogenide/silver image for subsequent etching by standard etching techniques.

A developing solution is made up as follows:  $K_2S_2O_5$ , 2 grams;  $Na_2SO_3$ , 8 grams;  $AgNO_3$ , 2 grams; water, 400 grams.

The wafer is immersed in the developing solution for 2 minutes while being flooded with radiation from an infrared lamp about 1 foot above the developing solution. The wafer is rinsed in water, after which it is placed under a collimated mercury lamp beam for a period of about 5 minutes. After this treatment the wafer is ready for etching. It is then inserted in a Tegal Plasma etcher with a  $CF_4$  flow adequate to provide a plasma with about 100 watts of rf energy. The wafer is fully etched in about 2 or 3 minutes to provide a high quality negative relief image.

The chalcogenide for this invention may be arsenic trisulfide or germanium-selenium or other glassy chalcogenide as desired. In general, arsenic trisulfide,  $As_2S_3$  is more commonly employed in the semiconductor art. The coating of this chalcogenide on the substrate is carried out slowly, at a steady rate, and at a low temperature. It has been found that coating at a rate of about 1 Å per second to about 2 Å per second is satisfactory. In the procedures described herein with arsenic trisulfide the coating operation is carried out by vacuum evaporation from an inert boat such as a molybdenum boat with a boat temperature of about 350°C, and different temperatures, of course, are used with other chalcogenides. Heat is supplied slowly and steadily to the boat, and evaporation speed is monitored by controlling the evaporation rate of the chalcogenide which in turn is controlled by the amount of heat supplied to the boat. Coating procedures are a significant factor in the sharply increased radiation response of the new system.

Alternatively, useful chalcogenide layers can be formed by other techniques such as chemical deposition and the like.

In the past, procedures generally known as photodoping have formed on a chalcogenide layer a silver image corresponding to a pattern as desired, and the silver has been driven into the chalcogenide by exposure to band-gap radiation or higher energy radiation such as visible light or ultra violet radiation. The term "band-gap radiation" as used here is well understood in the art to denote activating radiation of suitable type or wavelength to activate the material being treated. For silver doping of an arsenic trisulfide chalcogenide with a silver deposit on or near the surface thereof, band-gap radiation denotes a wavelength less than about 1/2 micron.

According to the present invention, a silver image for photodoping is formed on a chalcogenide surface and is then driven into the body in suitable ways such as, for example, as are illustrated in the following steps set forth in the above Example. As a first step, according to the Example, a layer of silver is placed on the chalcogenide. Various procedures for placing a silver layer on the chalcogenide are well known in the art and include both chemical reduction of silver from a solution of a silver salt onto the surface and vacuum evaporation. The presently preferred procedure is deposition from a solution of a silver salt.

The silvered chalcogenide element is then exposed in a suitable manner to a pattern which is to be replicated in the final product. This pattern in the semiconductor art may be a semiconductor circuit or other semiconductor element as desired; it may, for other arts, be any useful or decorative pattern as desired. According to previously known methods, exposure of a silver layer on a chalcogenide has an energy requirement in the order of 100-200 mJ per square centimeter in order to achieve a useful photodoping result. By contrast, according to the present invention, useful photodoping results are achieved through exposure of a silvered chalcogenide layer with an exposure of about 1 to 5 mJ per square centimeter. The exposure can be conventional exposure to visible light, to electron beam writing or to other band-gap radiation. Where extremely fine resolution is required, as in present semiconductor manufacturing operations, electron beam writing has been found to produce extremely fine resolution in the order of a wavelength of light.

After exposure, the excess silver or background silver is removed by suitable means. For example, the procedure shown in the above Example or other procedures may be employed.

Treatment of the silver-chalcogenide image is carried out with a silver-containing agent capable of depositing additional silver on the image areas. One such agent is  $\text{NaAgSO}_3$  as illustrated in the Example, and another is  $\text{NaAg}(\text{NO}_2)_2$ . The image chalcogenide is placed in contact with the silver-depositing agent. As shown in the Example, it is simultaneously exposed to radiation such as, for example, infrared radiation. Radiation other than infrared is also suitable, and generally it is desired to employ a wavelength less than about 1 micron. In the presently preferred embodiment of the invention the silver-depositing agent is  $\text{NaAgSO}_3$  and in the presence of infrared illumination the deposition of silver is carried out in less than about 5 minutes and, as shown in the Example, usually in about 1 or 2 minutes. In the absence of infrared radiation or similar radiation, using  $\text{NaAgSO}_3$  deposition is extremely slow and may require one or several hours. Another excellent silver-depositing agent is  $\text{NaAg}(\text{NO}_2)_2$ . Other silver agents have been found to deposit silver on the imaged chalcogenide, but not as satisfactorily as the preferred agents.

It is believed that the silver in the imaged chalcogenide prior to the treatment with the silver depositing agent is in the form of silver sulfide or a silver complex. It is believed that the silver-depositing agent acts to deposit additional silver on the sulfide and after this deposition begins, the agent then deposits silver on this silver deposit. Many silver-containing agents deposit silver on existing silver deposits, but do not deposit the additional silver on an image of silver sulfide or a silver complex.

Particularly where extremely fine resolution is desired, as in the semiconductor art, the silver deposited on the imaged chalcogenide should be in extremely fine form and not in larger crystal or agglomerate form. The preferred agent,  $\text{NaAgSO}_3$  deposits an extremely fine silver deposit, and is very suitable for resolutions in the order of a wavelength of light or a fraction of a wavelength.

After this deposition of silver imaging material from the sulfite or other bath, the strongly imaged chalcogenide is treated to drive the silver in the image areas into the chalcogenide body. As shown in the above Example, this can be accomplished by visible light. Where one is dealing with extremely fine patterns requiring extremely fine resolution, for example resolution in the order of the wavelength of light, collimated radiation is preferred, as it drives the silver more directly downward into the chalcogenide. A mercury vapor lamp is highly satisfactory, or other radiation of band-gap or shorter wavelength. The silver may be driven into the chalcogenide by heat or infrared radiation where such fineness of line is not required.

After silver doping, or driving the silver into the chalcogenide, the element is etched in a known manner, for example by means of an alkaline etch, a plasma etch or the like, forming a negative chalcogenide pattern on the substrate. This pattern is then ready for further use as desired. In particular, where a polymer resist layer on a semiconductor wafer underlies the chalcogenide, an oxygen plasma etch forms a resist pattern on the semiconductor wafer for further processing in semiconductor manufacture.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We have successfully Ag-photodoped $As_2S_3$ using photographic Ag derived from evaporated AgBr. The use of evaporated AgBr has resulted in a 1000-fold increase in speed. We have shown that evaporated AgBr has very high sensitivity in the deep UV (50 microJ/cm <sup>2</sup> at 2600Å), at soft x-ray wavelengths (5 microJ/cm <sup>2</sup> at 7Å) and confirmed the previously observed e-beam sensitivity of 10 <sup>-9</sup> coulombs/cm <sup>2</sup> . We have shown the feasibility of using evaporated AgBr as the photon sensitive layer of a multi-layer photoresist system for submicron lithography.		

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